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PATENT SPECIFICATION

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(19)

(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF SHAPED CARBON BODIES

(71) We, SIGRI ELEKTROGRAPHIT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, a German Company, of 8901 Meitingen bei Augsburg, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of carbon bodies from mixtures of carbon-containing solids and hardenable binders.

Masses for shaping to produce shaped carbon bodies are generally produced from mixtures of carbon-containing solids and binders. It is a feature of such masses that they generally consist of a mixture of solid and liquid phases. The solid phase can comprise petroleum coke, pitch coke, carbon black or graphite and is inert on carbonisation, having a content of fixed carbon of almost 100%. The liquid phase owes its presence to the binder used which can consist of coal tar pitch or synthetic resins and which contains considerable quantities of volatile carbon compounds. To achieve almost 100% content of fixed carbon throughout the shaped carbon bodies, carbonisation of the binders must be effected. The consequent splitting off of the volatile compounds during the carbonisation treatment, results in tensile stresses being set up at the phase boundaries. These stresses initiate formation of cracks which are detrimental to the quality of the shaped bodies and may result in complete destruction of the bodies. In order to reduce the magnitude of these harmful, stresses, attempts have been made to use pitches and resins with low contents of volatile substances, as binders. However, such binders have insufficient pliability and wettability, so that shaped masses for carbonisation could not be produced.

In order to overcome this problem, it has been proposed in German Patent Specification No. 1,113, 214, to produce a single phase carbonisable shaped mass from which carbon and graphite bodies of a low gas permeability can be produced. The single phase mass is produced by suspending in water cellulose ground to extremely fine form, dehydrating the suspension obtained to produce a shaped mass and carbonising or graphitising the shaped mass by slow heating with exclusion of air. Owing to the two-stage heating procedure involved, it is not possible to produce shaped bodies of accurate dimensions by this method. Dehydration of the suspension results in shrinkage of about 50% occurring and the subsequent carbonisation results in shrinkage by about 32%.

According to one aspect of this invention, there is provided a process for the production of a shaped carbon body, which comprises shaping a mixture of a powdered or chip-form carbon-containing solids component which can be transformed into carbon without passing through a liquid or plastic phase, by heating in an inert atmosphere and a carbon-containing liquid synthetic resin which forms a solid infusible mass under the action of heat or catalysts and subjecting the shaped mass obtained to a carbonisation heat treatment in an inert atmosphere, the solids component and liquid synthetic resin both undergoing weight losses of from 40 to 60% during the carbonisation heat treatment.

According to a second aspect of this invention, there is provided a composition suitable for use in the process of this invention for the production of a shaped carbon body, comprising a powdered or chip-form carbon-containing solids component which

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can be transformed into carbon without passing through a liquid or plastic phase, by heating in an inert atmosphere and a carbon-containing liquid synthetic resin which forms a solid infusible mass under the action of heat or catalyst, the resin and the solids component both undergoing weight losses of from 40 to 60% when subjected to a carbonisation heat treatment.

This invention is based on the discovery that, the formation of quality-reducing cracks during the carbonisation of a two phase shaped mass can be avoided if the solids and liquid synthetic resin used as binder in the shaped masses both undergo shrinkage to a similar extent during carbonisation of the resin. The solids and resin will generally both shrink by the same amount in all directions. Shaped bodies produced according to the invention are free from internal stresses and present a uniform structure similar to that of glass-like carbon. They remain substantially unaffected by change in temperature. Since the solids and resins will generally shrink by the same amount in all directions the process is reproducible and shaped bodies of any kind and also of relatively large dimensions can be produced to accurate dimensions.

The solids and resins used will preferably undergo the same percentage loss in weight. Solids which will undergo shrinkage during carbonisation of the binders will generally undergo carbonisation themselves, but will not yield volatile cleavage products to the same extent as the resins, if they yield volatile cleavage products at all. Such solids will generally comprise cellulose, such as sawdust, and/or ground hardened synthetic resins.

Preferred resins for use in the process according to the invention are hardenable synthetic resins, such as phenol formaldehyde resins, furan resins or mixtures of these resins.

Carbon bodies of lower fluid permeability can be obtained, if according to a preferred embodiment of the invention, the shaped masses are coated before the carbonisation stage with a film consisting of hardenable synthetic resin which, when carbonised forms a vitreous carbon layer which resin undergoes weight loss of from 40 to 60% during the carbonisation heat treatment. The use of phenol formaldehyde resins, furan resins or a mixture of these resins if preferred. The thickness of the synthetic resin film is preferably less than 1 mm.

Hardening, cross-linking and carbonising of the film coating yields a carbon coating of a glass-like appearance.

Since the films are formed of the same types of material as the binder resin, they show the same shrinkage behaviour as the shaped bodies during hardening and carbonisation, so that stresses in the boundary region between synthetic resin film and basic body are avoided during the heating process.

When carrying out the process according to the invention, the solids material in powder or chip form, generally after a suitable drying treatment in the case of cellulose-containing materials is liquid synthetic resin, and formed into the desired shape. The two phase mixture of solids and resin binder will generally be of such a consistency as to permit the spreading thereof on a support e.g. by trowelling. Alternatively, the required shaped mass for hardening and carbonisation can be formed by pressing or vibrating.

The resin binder is thereafter hardened by heating the shaped mass to 100 to 200°C and the shaped masses are then carbonised by further heating in an inert atmosphere to 800 to 1000°C. The rise in temperature between 350 and 600°C will generally be at a rate of from 3 to 4 C/h. The linear shrinkage during the carbonisation is about 22%. If desired, the carbonised bodies can be graphitised by further heating to temperatures of at least 2500°C, the shaped bodies then shrinking by 6 to 7%. When hardened resins are to be used as solids material, a hardenable synthetic resin, for example phenol formaldehyde resin or a furan resin is heated in a mould to a temperature of about 200°C and the solid resin mass thereby formed is ground after cooling to room temperature.

In order to produce shaped carbon bodies of increased fluid impermeability as mentioned hereinabove, synthetic resins, which can contain hardening catalysts, are sprayed or brushed on to carbon-containing shaped masses which have been hardened by heating usually at a temperature of from 100 to 200°C. The synthetic resin film is then hardened by a further heating of the masses usually to a temperature of from 100 to 200°C and is then carbonised together with the basic shaped carbon mass as aforesaid possibly followed by graphitisation. A layer of glass-like carbon is formed from the synthetic resin layer. The carbon layer has a very low permeability and adheres to the basic material.

The carbon or graphite bodies produced by the process according to the invention are particularly suitable for use as refractory linings, linings of electrolysis cells and furnace insulations. These shaped bodies which are coated with synthetic resin films and thereafter carbonised to render them practically impervious to liquids and gases have the further property that the glass-like surface layer, when produced, has a very high resistance to wear and is very stable with respect to oxidising substances. Such coated carbon bodies are thus particularly suitable for use as electric contacts, electrodes, linings of chemical apparatus and metallurgical vessels, and as

P.B.5818 - Patentlaan 2
2280 HV Rijswijk (ZH)
☎ +31 70 340 2040
TX 31651 epo nl
FAX +31 70 340 3016

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European Patent Office
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HOFFMANN - EITLE
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München
ALLEMAGNE

EINGEGANGEN
24. Nov. 2003
HOFFMANN • EITLE, MÜNCHEN
PATENTANWÄLTE RECHTSANWÄLTE

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Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire
Toshiba Ceramics Co., Ltd.

COMMUNICATION

The European Patent Office herewith transmits as an enclosure the European search report for the above-mentioned European patent application.

If applicable, copies of the documents cited in the European search report are attached.

[X] Additional set(s) of copies of the documents cited in the European search report is (are) enclosed as well.

The following specifications given by the applicant have been approved by the Search Division:

[ ] abstract [X] title

[X] The abstract was modified by the Search Division and the definitive text is attached to this communication.

The following figure will be published together with the abstract: NONE

REFUND OF THE SEARCH FEE

If applicable under Article 10 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 13 0293

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X Y	US 6 051 096 A (BYRNE CHRISTOPHER E ET AL) 18 April 2000 (2000-04-18) * abstract * * column 8, line 51 - line 58 * * column 14, line 59 - line 62 * * column 40, line 18 - column 44, line 24 * * column 44, line 60 - column 45, line 29 * * claims 49-52 *	1,5-10 4,8	C04B35/573
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 11, 30 September 1999 (1999-09-30) & JP 11 147779 A (TOSHIBA CERAMICS CO LTD), 2 June 1999 (1999-06-02) * abstract *	4	
Y	DE 21 31 792 A (SIGRI ELEKTROGRAPHIT GMBH) 28 December 1972 (1972-12-28) * page 3, line 6 - line 12 * * claim 3 *	8	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C04B C09J
A	SHIN D-W ET AL: "SILICON/SILICON CARBIDE COMPOSITES FABRICATED BY INFILTRATION OF A SILICON MELT INTO CHARCOAL" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, AMERICAN CERAMIC SOCIETY. COLUMBUS, US, vol. 82, no. 11, November 1999 (1999-11), pages 3251-3253, XP000862734 ISSN: 0002-7820 * the whole document *	1-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 October 2003	Burtan, M-M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
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